

COMBINED REMOTE LIBS AND RAMAN SPECTROSCOPY MEASUREMENTS

J. Thompson¹, R. Wiens¹, S. Sharma², P. Lucey², A. Misra²; ¹Space Science and Applications, Los Alamos National Laboratory, MS D-466, Los Alamos, NM 87545, USA; (justint@lanl.gov), ²Hawaii Institute of Geophysics and Planetary Science, University of Hawaii 2525 Correa Rd. HIG, Honolulu, HI 96822, USA

Overview: Laser-Induced Breakdown Spectroscopy (LIBS) and Raman spectroscopy (RS) are very complementary techniques. RS yields information about minerals and their polymorphs, and also identifies organic molecules from vibrational spectra. LIBS yields detailed information on elemental compositions, including many minor and trace elements. Here we present a combined data set of remote LIBS and RS measurements, showing how they complement each other.

Introduction: Recent work has discussed combining these techniques, and provided a few examples of their complementarity. Burgio et al. [1] used the combination to provide in-situ analyses of paint pigments in a historic art work. Wiens et al. [2] discussed the feasibility of constructing an instrument, suitable for spaceflight, that would be capable of both techniques. Recent papers have demonstrated the feasibility of using both techniques at stand-off distances, including using remote RS to distinguish coral from calcite, which looked identical to LIBS, and using LIBS to determine the Fe/Mg ratio of an olivine and the Mg/Ca ratio of a dolomite, which can be difficult for RS [3-4].

Experimental Setup: The experimental set-up for the remote Raman system used a Big Sky Nd:YAG laser, frequency doubled to 532 nm at 20 Hz. The signal was collected with a 125 mm diameter reflecting telescope, coupled to a Raman Holospec spectroscope through a 100 μ m slit after passing through a holographic super-notch filter to remove incident laser light [3]. The spectrograph was coupled directly to the telescope without passing the light through an optical fiber. The detector was an intensified CCD detector from Princeton Instruments. For details of the directly coupled remote Raman set up see Misra et al. [4].

The LIBS set-up used a Surelite Continuum Nd:YAG laser, also frequency doubled to 532 nm at 20 Hz, with a maximum power of 35 mJ. (This laser was used for convenience). A 5x beam expander was placed in front of the laser, with the light focused on the sample, at a distance of 8.3 m. The return light was collected by a 10.8 cm diameter Newtonian reflecting telescope without a glass window, and was focused into a 200 μ m diameter optical fiber. The fiber alternately fed the light into one of two Ocean Optics HR2000 spectrometers configured for 225-320 nm ("UV unit") and 385-460 nm ("VIS unit") wavelength ranges. These are similar in their optical properties to the units to be flown on the ChemCam LIBS instrument on MSL. A third spectral range was provided by the remote RS system's telescope and Holospec spectroscope. The integration times were 3 and 10 seconds for the VIS and UV spectrographs, and 30 sec at a gain of 150 for the Holospec/ICCD. LIBS and RS data were

obtained sequentially, as each technique requires a significantly different laser power density at the target. The LIBS spot size with this setup was \sim 600 μ m, whereas the Raman spot size was \sim 1 cm.

Samples: We chose to compare two sets of calcium-bearing minerals: anhydrite (CaSO_4) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), two sulfates which differ in their major chemistry only by the presence of water, and dolomite ($\text{CaMg}(\text{CO}_3)_2$) and diopside ($\text{CaMgSi}_2\text{O}_6$). In both sets, the cation major element chemistry is identical.

Results: The work presented here shows the ability to combine remote LIBS and Raman spectroscopy in order to infer cationic composition and mineralogy on planetary surfaces.

Fig. 1A shows the LIBS spectra of anhydrite and gypsum in the range of 240-720 nm. The major cation in these two minerals is calcium, and calcium lines dominate the two spectra. The LIBS spectrum was recorded in the air, and no sulfur peak was observed. Sulfur lines are observed in LIBS spectra measured under low CO_2 atmosphere [7] similar to on Mars. In the LIBS spectrum, the presence of hydrogen is indicated by a broad line 656 nm. The LIBS spectrum of gypsum, which has water crystallization, displays the H line, distinguishing it from anhydrite. The spectrum of anhydrite also indicates the presence of trace Li (670.8 nm), Na (589 nm), Sr (407.8, 421.6 nm), and Mg (280, 285 nm).

The Raman spectra of anhydrite and gypsum are seen in fig. 1B. Strong lines at 1018 cm^{-1} and 1014 cm^{-1} are observed in the Raman spectra of anhydrite and gypsum, respectively. These lines are Raman fingerprints of SO_4 ions, and correspond to the symmetrical stretching mode of oxygen of SO_4 ions. The regions of 400-500 cm^{-1} , 600-700 cm^{-1} , and 1100-1200 cm^{-1} show internal modes of SO_4 ions. The lines at 1558 cm^{-1} and 2333 cm^{-1} are symmetrical stretching modes of atmospheric oxygen and nitrogen, respectively. In the Raman spectrum of gypsum, two strong lines are observed at about 3400 cm^{-1} and 3500 cm^{-1} (not shown in figure 1b). These two lines correspond to $\nu(\text{O-H1})$ and $\nu(\text{O-H2})$ modes of water molecules [8]. No such band is observed in the spectrum of anhydrite indicating that anhydrite does not have water in its structure. The fingerprints of the SO_4 ions and O-H stretching modes in the spectra of these two minerals can be used to identify unknown SO_4 containing minerals. The bands in the O-H stretching region can be used to discriminate between hydrous and anhydrous minerals.

Although indirect information about the major cations can be obtained from the position and splitting of normal lines, the Raman spectra do not provide any information about trace elements that may be present. By combining LIBS and Raman results, it is possible to provide complete

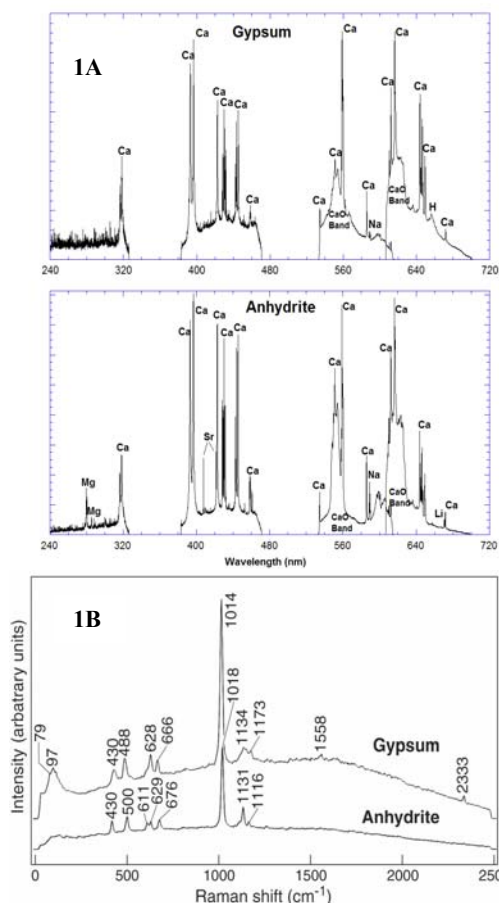


Fig.1: (A) LIBS spectra (B) Raman spectra of gypsum and anhydrite.

information about elemental composition and mineral structure.

The LIBS spectra of dolomite ($\text{CaMg}(\text{CO}_3)_2$) and diopside ($\text{CaMgSi}_2\text{O}_6$) are shown in fig. 2A in the range from 240-720 nm. The two major cations in these two minerals are Ca and Mg, and these lines dominate the two spectra. The weak C emission line at 247.7 nm is apparently just below the detection limit under these conditions, for the dolomite sample. Both samples show Si emission lines at 288.2 and 251-253 nm, though these lines are much less prominent in the dolomite sample, and must represent a minor phase. The dolomite sample also shows Li, and relatively strong Sr and Ba (455.4 nm) peaks, characteristic of carbonate.

In the Raman spectrum of dolomite, the symmetrical stretch of carbonate ions is at 1097cm^{-1} . The band at 723cm^{-1} and 1443cm^{-1} correspond to symmetrical banding and atisymmetric stretch of carbonate ions. The weak band at 1761cm^{-1} [6] is a combination mode. The low frequency bands at 176cm^{-1} and 300cm^{-1} are characteristic of dolomite lattice modes. On the basis of lattice and internal modes of Raman active vibrations, carbonate

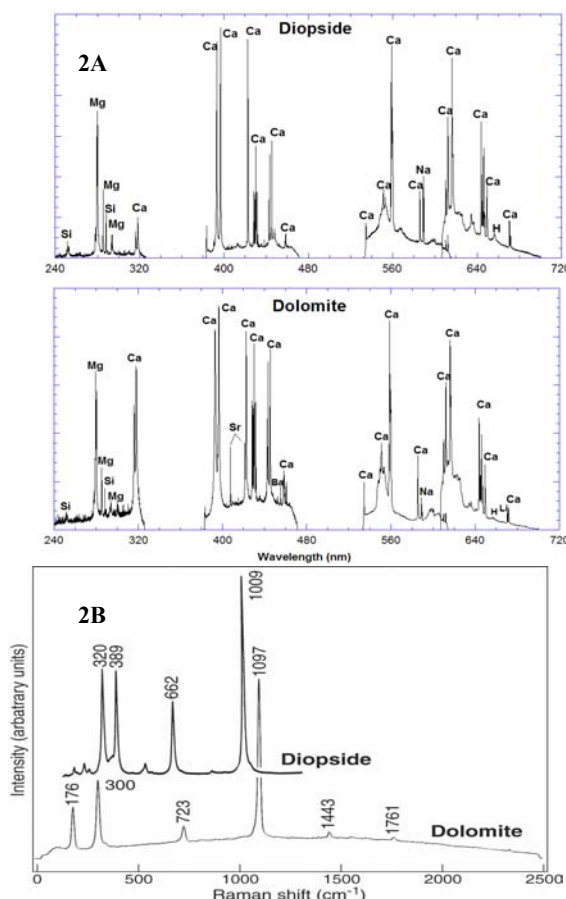


Fig. 2: (A) LIBS spectra (B) Raman spectra of diopside and dolomite.

minerals can be identified.

As discussed before, the LIBS spectra provide information about the presence of minor cations. Interestingly no Raman band characteristic of silicate was observed in the dolomite Raman spectrum, indicating that the contaminates are not homogeneously distributed in the dolomite crystal.

The Raman spectrum of diopside in fig. 2B shows two strong bands at 662cm^{-1} and 1009cm^{-1} . The 662cm^{-1} Raman band is the fingerprint of a pyroxene silicate chain. This band corresponds to symmetrical stretching of bridging oxygen ($\nu_s(\text{Si-O-Si})$). The 1009cm^{-1} band corresponds to symmetrical stretching of nonbridging oxygen ($\nu_s(\text{Si-O}^-)$). These bands can be used to determine the presence of pyroxenes on planetary surfaces. By combining LIBS (fig. 2A) with Raman spectroscopy, we could obtain information both on the major and minor cationic composition and mineral phases.

References: [1] Burgio, L. *et al.* (2000) *Appl. Spectrosc.* 54, 463-469. [2] Wiens, R.C. *et al.* (2000) *Lunar Planet. Sci. XXXI*, 1468-1469. [3] Hubble, H.W. *et al.* (2002) *Lunar Planet. Sci. XXXIII*, 1935. [4] Misra, A.K. *et al.* (2004) *Geo-Raman 200*, Abstracts SOEST-04-02, 45-46. [5] Sharma, S.K. *et al.* (2003) *Spectrochim. Acta A* 59, 2391-2407. [6] Sallé B. *et al.* (2004) *Spectrochim. Acta B* 59, 1413-1422. [7] Chio *et al.* (2003) *Applied Spectrosc.* 57, 774-783.